applied sciences

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First Example of Unsaturated Poly(Ester Amide)s Derived From Itaconic Acid and Their Application as Bio-Based UV-Curing Polymers

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Received: 21 January 2020; Accepted: 14 March 2020; Published: 22 March 2020

Abstract: Recently, itaconic acid has drawn considerable attention as a novel radical-curing building block for polyester resins. These bio-based materials have been used in thermal, as well as ultra violet (UV) curing applications, such as printing inks or coatings. Poly(ester amide)s from itaconic acid could be very interesting, as the amide group could alter the properties of the resins as well as cured materials. However, standard polycondensation reactions with diamines are not possible with itaconic acid as the amines preferably react via an aza-Michael addition at the α,β-unsaturated double bond. Therefore, alternative and more elaborate synthetic strategies have to be developed. Herein, we present two different synthetic strategies to poly(ester amide)s from itaconic acid that circumvent the addition reaction of the amines. This is in both cases done by a pre-reaction to form stable amide building blocks that are then reacted with itaconic acid or polyesters derived thereof. The structural composition and the properties of the resin are characterized, and the UV-curing reactivity is examined. All properties are compared to corresponding polyesters from itaconic acid.

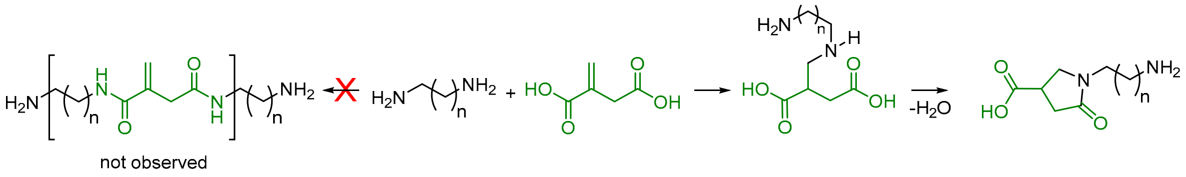
Keywords: poly(ester amide)s; UV-curing polymer resins; photo-DSC; itaconic acid; bio-based polymers

1. Introduction

Over the last decade, immense research efforts have been undertaken to implement bio-based monomers as suitable alternative building blocks in polymeric materials [1–4]. This is mostly driven by the imminent scarcity of fossil resources, as well as the enormous potential to exploit local resources and therefore reduce the dependency on imported fossil fuels. In addition, increased public awareness and the desire to move towards a more sustainable economy also create an incentive to find material solutions from renewable resources. However, besides the sustainability aspect, novel bio-based building blocks may also exhibit unprecedented structural features that are not economically accessible from petrochemical feedstock. This, in turn, can lead to new materials with improved properties.

Itaconic acid (IA), also known as methylene succinic acid, has drawn considerable attention in this context over the last few years [5]. This unsaturated dicarboxylic acid is commercially available in larger quantities (>80.000 t/a) at a competitive price (<2 €/kg). It is biotechnologically produced by fermentation of sugar or molasses with the fungi aspergillus terreus [6–8]. The three functional groups allow for the exploitation of itaconic acid in several different chemical transformations to obtain novel monomeric structures. As far as polymer chemistry is concerned, mainly two different classes of polymers derived from itaconic have been intensively studied. The α,β-unsaturated double bonds, allows for radical polymerization reactions, which has been exploited in several homopolymers and co-polymers of itaconic acid with a range of applications [9–13]. As a second pathway, the two carboxylic acid groups allow for polycondensation reactions to obtain polyesters [14–20]. These have been used as reactive binder resins for coatings, shape-memory materials, printing inks, etc. [21–25]. In addition, these polyesters have been exploited in post-polymerization modification reactions to obtain new polymeric structures [26–29].

However, to date, no examples of unsaturated poly(ester amide)s based on itaconic acid have been reported. This is mostly due to the fact that the synthesis of these polyester amides is by no means straightforward. The biggest challenge during a standard polycondensation reaction is the nucleophilic attack of the diamine at the α,β-unsaturated double bond. This aza-Michael addition was first reported by Paytash et al. in 1950, and it was shown that subsequently leads to the formation of pyrrolidone rings (Scheme 1). [30] Later, this ring-closing reaction was exploited for the synthesis of several bio-based polyamides [31] and poly(ester amides). [32] However, polymers of this type cannot be utilized in radical curing reactions, as the aza-Michael addition results in complete consumption of the unsaturated double bond.



Scheme 1. Aza-Michael addition with subsequent ring-closing to the pyrrolidone ring.

Therefore, more sophisticated synthetic procedures have to be developed in order to synthesize poly(ester amide)s derived from itaconic acid without the consumption of the unsaturated double bond. This class of unsaturated polymers is of high interest as the amide groups can have a considerable impact on the properties of the materials before and after curing. Herein, two different synthetic strategies are presented that allow for the synthesis of unsaturated aliphatic poly(ester amide)s from itaconic. To the best of our knowledge, this is the first example of this kind of polymeric resins. In addition, the materials are characterized and examined on their suitability to be utilized as UV-curing polymers in coating applications.

2. Experimental

2.1. Materials

As an azeotropic solvent, toluene (technical grade) was utilized, which was received from VWR international and purified by distillation. Itaconic acid (99%) was purchased from ECEM. 1,6-hexanediol (97%) was obtained from Dr. Lobinger Chemie, adipic acid (99%) from Acros. 3,5-Di-tert-butyl-4-hydroxytoluene (Butylated hydroxytoluene (BHT), 99%) and 4-methoxyphenol (MeHQ, 98%) were received from Fluka Analytical. Titanium butoxide (97%) and zinc acetate dihydrate (99%) were obtained from Sigma Aldrich. Hexamethylenediamine (>99%), ethane-1,2-diol (>99%) were purchased from Fluka. Irgacure 1173 was obtained from BASF. FASCAT 4101 was provided by FASCAT Catalysts. All reagents were used without further purification.

2.2. Methods

The acid value (AV) corresponds to the non-reacted acid groups. It was defined as the number of milligrams of potassium hydroxide required to neutralize 1 g of sample and was determined according to DIN EN ISO 2114 by titrating the remaining carboxylic acid groups of the sample with a solution of potassium hydroxide in methanol (0.3 mol/L).

UV-curing: For a typical curing experiment, 5% of the photoinitiator (Irgacure 1173) was added to the resin and mixed until a homogenous liquid was obtained. To reduce air bubbles that have been formed as a result of the mixing, the resin was heated to 50 °C for one hour. The UV-reactive mixture was then applied on a glass plate with the aid of a metal squeegee with a gap size of 150 µm. For the curing of the films, a Technigraf 8 Amp equipped with a UV 4/120-2 light (254 nm) UV-oven was used. The speed of the conveyor belt was set to 5 m/min. To ensure a consistent radiation dose, the intensity of the oven was measured before and after curing, resulting in average intensity of 500 mJ/cm^2. In addition to the films cured, the reactivity of the materials towards UV-induced radical crosslinking was assessed by photo-DSC.

2.3. Measurements

Nuclear magnetic resonance (NMR) experiments were measured at 400 MHz for ^{1}H NMR on a Bruker Avance III 400-MHz spectrometer (Bruker, Billerica, MA, USA). Proton shifts are reported in ppm (δ) downfield from TMS and were determined by reference to the residual solvent peak ($CHCl_3$, 7.26 ppm for hydrogen atoms). A Mettler Toledo DSC^{3+} STARe System was used for the Photo-DSC measurements. The system is equipped with a Lightning Cure LC8 lamp, which was set at 70% of its intensity. The measurements were conducted in 40 µL crucibles without lids. Two similar runs were conducted with a 30 s break between the two runs. This was done to be able to obtain the integration of signal only without the influence of the lamp. To get the value of the heat generated during the curing, the second curve was subtracted from the first. Each run was conducted as follows: 30 s at 25 °C, at atmospheric pressure under air with the lamp turned off, then the lamp is started for 10 min. The break between the curing runs lasts 30 s. A Thermo Scientific Nicolet iS5 FT-IR (Thermo Fischer Scientific, Waltham, MA, USA) was used to obtained infrared spectroscopy. Viscosity measurements were conducted on a Bohlin CVO 120 Rheometer. The machine was equipped with a PP40 disc (CP 4°, 40 mm). Measurements were taken with a shear rate of 50 s^{-1} for 10 s. For each temperature (25, 37.5, 50, 62.5, 75 °C), five measures were taken and the average value was calculated for each temperature. A Malvern Viscotek GPCmax was utilized to for size-exclusion chromatography (SEC). The instrument is equipped with triple detection, consisting of a Schambeck RI2012, a refractive index detector, and a Malvern Dual detector. Two PLgel 5 mm MIXED-C, 300 mm columns from Agilent Technologies at 35 °C were utilized for the separation. Chloroform (CHROMASOLV, for HPLC, >99.8%) was used as the eluent at a flow rate of 1.0 mL min^{-1}. Data acquisition and calculations were performed using Viscotek OmniSec software version 5.0. The samples were filtered over a 0.2 mm polytetrafluorethylene (PTFE) filter prior to injection.

2.4. Synthesis of Bio-Based Oligoester (OE)

Typically, itaconic acid (1 eq), 1,6-hexanediol (1.25 eq), BHT (400 ppm) and MeHQ (300 ppm) as the free radical polymerization inhibitors were charged into a three-necked round-bottomed flask, which was equipped with a mechanical stirrer and a Dean-Stark apparatus. Using toluene as entrainer, the mixture was heated to 130 °C and kept at this temperature until the complete melt of the monomers. Then the catalyst, zinc acetate (0.4%), was added, and the mixture was stirred at 180 °C. The course of the reaction was tracked by the analysis of the acid value (AV). When the AV reached a value of less than 5 mg KOH/g, the toluene was removed under reduced pressure. The polyester was obtained without any further purification as a yellow viscous liquid.

2.5. Oligoesteramidesynthesis (OEA)

For the oligo(ester amide) (OEA) synthesis, 5 g (28.7 mmol) of adipic acid (AA), 4.98 g (80.36 mmol) of ethylene glycol (EG) and 0.66 g (5.74 mmol) of hexamethylene diamine (HMDA) with 0.1% (wt%) of zinc acetate were charged into a two-necked round-bottomed flask. Then the mixture was heated to

190 °C under a stream of nitrogen for 2 h. After cooling, the excess of EG was removed by extraction with dichloromethane. The OEA was obtained as a very viscous white liquid.

2.6. Transesterification to the Poly(Ester Amide)s (PEAs)

For all transesterification reactions, the OE and a given percentage of OEA (in mol%) were placed in a two-necked round-bottomed flask and (0.1% wt%) of $Ti(OBu)_4$, 150 ppm of MeHQ and 100 ppm of BHT were added. Then the reaction mixture was slowly heated to 160 °C under a stream of nitrogen for 4 h. The PEAs were obtained as brown viscous liquids.

2.7. Pseudo One-Pot Synthesis of Poly(Ester Amides)

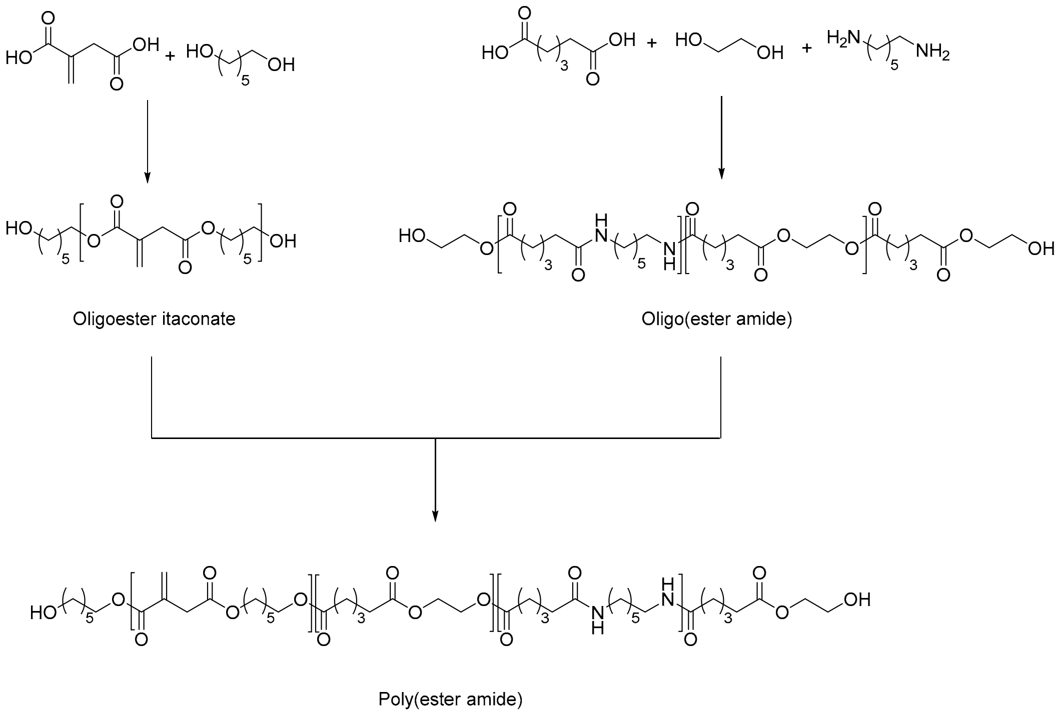
In a first step, hexamethylene diamine was reacted under nitrogen with an excess of dimethyladipate at 150 °C in the presence of 0.1 wt% of $Zn(OAc)_2$ as a catalyst to obtain bis(esteramide)s. The consumption of the amine was monitored by means of ATR-FTIR. After the complete consumption of the free amines, a white waxy solid was obtained. Then itaconic acid, 1,6-hexanediol, BHT (400 ppm), MeHQ (300 ppm), and Fascat 4101 (0.4 wt%) were added, and the flask was equipped with a mechanical stirrer and a Dean–Stark apparatus. Using toluene as the entrainer, the mixture was slowly heated to 180 °C. The course of the reaction was monitored by analysis of the acid value (AV). When the AV reached a value of less than 5 mg KOH/g, toluene was removed under reduced pressure. The poly(ester amide)s were obtained without any further purification as yellow viscous liquids.

3. Results and Discussion

As discussed in the introduction, the biggest challenge in the synthesis of unsaturated poly(ester amides) derived from itaconic acid is the undesired aza-Michael addition of the diamine at the α,β-unsaturated double bond of the itaconic acid. To solve this synthetic problem, two different strategies have been investigated in the course of this study: (1) A first one, based on a transesterification approach and (2) another one based on an in-situ formation of a bis(ester amide).

3.1. Synthesis of Poly(Esteramide)s Via Transesterification Approach

For the transesterification approach, a standard oligoester itaconate (OE) and an oligo(ester amide) (OEA) were synthesized separately. Then, the desired poly(ester amide) was obtained by a transesterification reaction of the two oligomers. This synthetic protocol should prevent the formation of free amines during the final step due to the high stability of the amide bond, resulting in the suppression of the undesired side-reaction. The complete synthetic strategy is shown in Scheme 2. It is noteworthy to mention that a high conversion of the transesterification is necessary to ensure that all polymer chains have a sufficient amount of unsaturated bonds. This is important to obtain materials that are reactive enough towards UV-induced radical crosslinking.



Scheme 2. Overall synthetic pathway to itaconic acid-based poly(ester amide)s (PEA)s.

The synthesis of the itaconic acid-based OE was conducted as described in previous studies [20,25]. A ratio of 1.25:1 (HDO:IA) was chosen to obtain an OE with a lower molecular weight distribution usually used in UV-curing resin applications.

The synthesis of the OEA was not straightforward. In the first set of experiments, dimethyl succinate was reacted with hexamethylene diamine (0.2 eq.) and an excess of ethylene glycol (2.8 eq). However, the use of the succinate leads to the formation of a substantial amount of succinimide instead of the desired oligo amide (see SI for details and spectra). Therefore, the synthesis was then conducted starting from dimethyl adipate, as here, the formation of an imide is not possible. An excess of glycol was used to obtain an OEA with low molecular weight, and therefore, low viscosity suitable for resin applications. In addition, the excess ensured that the oligomers were OH-terminated to avoid any free amine groups in the final products, as these would again lead to undesired side-reactions during the transesterification step. After the reaction, the OEA was purified by extraction with dichloromethane to remove unreacted ethylene glycol and small dimeric ester fractions. Removal by distillation was not desired, as this would lead to further polymerization of the OEA. The NMR spectra of the OEA obtained was free of unreacted ethylene glycol. The amount of amide in the oligomer was found to be 14%, which was determined by integration of the CH_2-signals next to the ester or amide bond, respectively (6 and 6′′ for the ethylene glycol esters and three for the amide, see Figure 1b). The OEA was obtained as a white waxy solid.

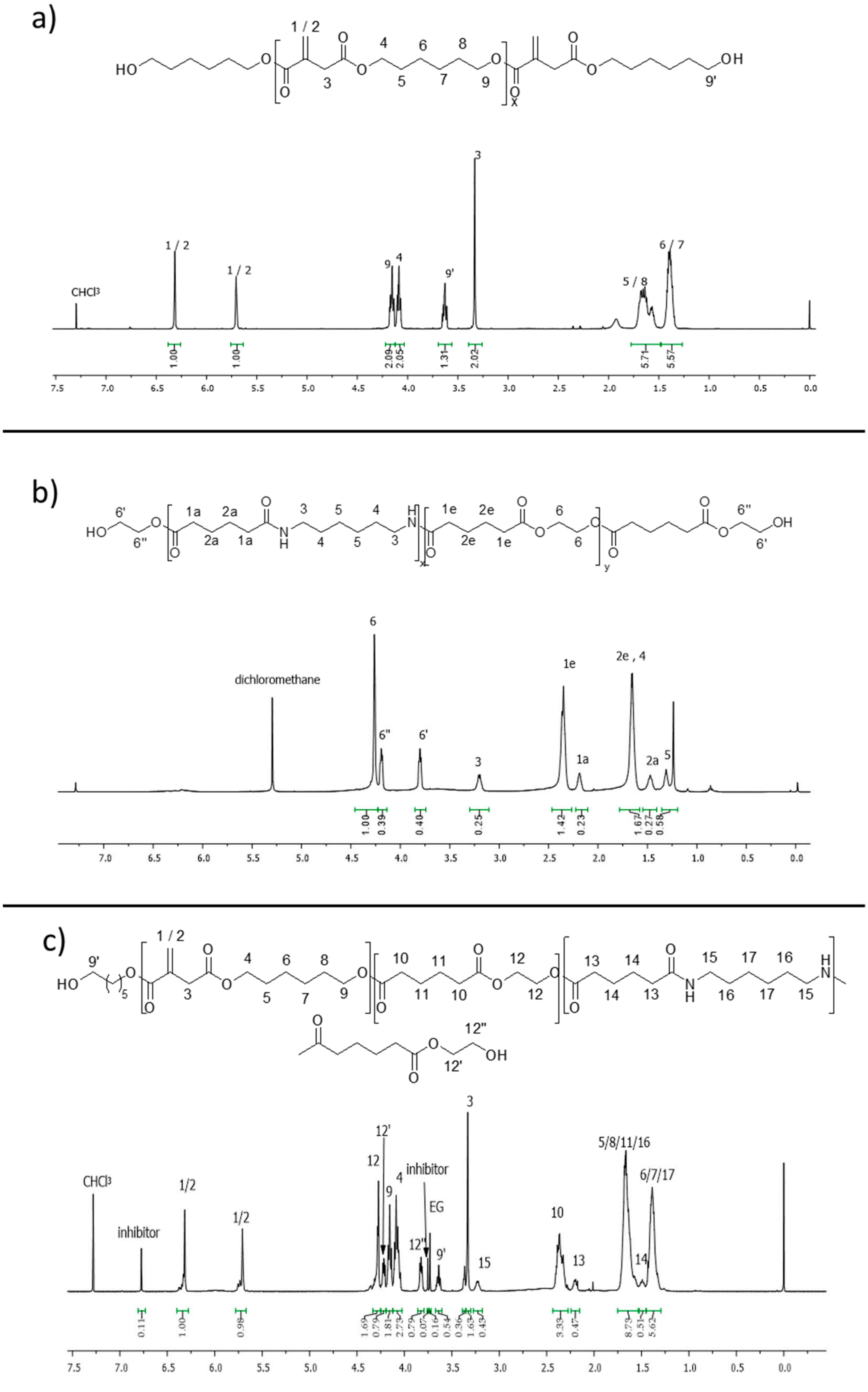


Figure 1. ^{1}H NMR spectra of a) Oligoester (OE), b) Oligoester amide (OEA), c) and PEA-005.

In the last step, the OE was reacted with the OEA in different ratios (95/05 to 60/40, see Table 1). In this transesterification step, the two oligomers were heated to 160 °C in the presence of $Ti(OBu)_4$ as a catalyst. The reaction was conducted under ambient pressure to avoid removal of ethylene glycol from the system, as this would lead to an increase in molecular weight. This was not desired, as the co-polymers should exhibit low enough viscosities that are compatible with coating applications. The percentage of amide in the final co-polymer was calculated from the integrals of the NMR signals corresponding to the ester and amide groups.

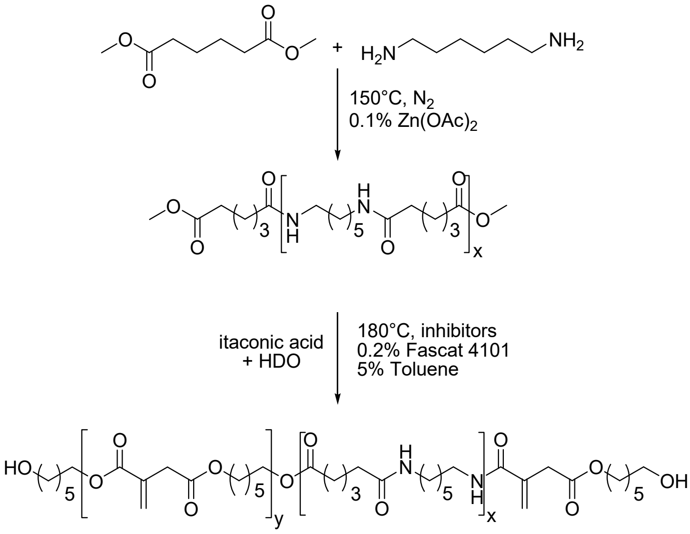
Table 1. Different compositions and amide content of the PEAs synthetized via the transesterification method.

Sample	PEA Composition OE/OEA	% Amide (Theoretical)	% Amide [a] (Determined)
PEA-001	95/5	0.7	n.d. [b]
PEA-002	90/10	1.4	2.1
PEA-003	80/20	2.8	2.5
PEA-004	70/30	4.2	4.0
PEA-005	60/40	5.6	5.7

[a] Calculated by the ratio of the ester to amide bonds determined by means of ^{1}H NMR; [b] due to the low intensity of the amide signals, a reliable integration was not possible.

3.2. Synthesis of Poly(Esteramide)S Via In-Situ Formed Bis(Ester Amide)s

As a second possibility, to circumvent the aza-Michael addition, a pseudo-one-pot reaction was conducted. For this, HMDA was first reacted with an excess of dimethyl adipate until all amine groups were reacted to the corresponding amide, which was followed by FT-IR. Then, itaconic acid and HDO were added, and the polycondensation was performed under standard conditions (Scheme 3). Following this procedure, three PEAs (PEA 101–103) with different amounts of HMDA and, in turn, different percentages of amide content have been synthesized (Table 2). Again, the feed ratio of the amine was compared to the composition determined by means of NMR. However, in this case, the measured amide content is higher for PEA 101 and 102.



Scheme 3. Synthesis of PEAs via pseudo-one-pot approach.

Table 2. Different compositions and amide content of the PEAs synthesized via the pseudo one-pot approach.

Reference	IA	DMA	HMDA	HDO	% Amide (Theoretical)	% Amide [a] (Determined)	% Isomerization [b]
PEA-101	0.8	0.2	0.068	1.282	2.9	3.8	22
PEA-102	0.7	0.3	0.13	1.22	5.4	7.1	6
PEA-103	0.5	0.5	0.23	1.12	9.1	8.4	40

[a] Calculated by the ratio of the ester to amide bonds determined by means of ^{1}H NMR; [b] Calculated by ratio of the olefinic protons of itaconic and mesaconic acid moiety determined by means of ^{1}H NMR.

3.3. IR and NMR Analysis

The synthesized copolymers were characterized by FTIR and ^{1}H NMR to confirm their molecular structures. The FTIR spectra of all PEAs (supplementary materials, Figures S4–S18) clearly show the characteristic absorption band for ester carbonyl stretching at 1732 cm^{-1}. In addition, the stretching and deformation bands of the conjugated double bond can be found at 1631 cm^{-1} and 814 cm^{-1}, indicating that the unsaturated double bond does not get attacked during the reaction. For PEAs with higher amide content, the FTIR spectra show two small vibrations at 1538 and 3306 cm^{-1}, corresponding to the amide and the N-H bonds.

The ^{1}H NMR spectra exhibit all the characteristic signals for PEAs from itaconic acid. Fo series one, the transesterification can be witnessed by a change of the signals compared to the virgin polyesters and oligoamides (Figure 1). During the transesterification step, the terminal OH-groups of the hexanediol undergo a nucleophilic attack on the ester bonds of the oligoamide. As a result, the signals of the CH_2 of the terminal hexanediol (signal 9′ at 3.65 ppm) are being reduced with the increasing amount of oligoamide. In addition, the ratio of the CH_2 signals of the hexanediol next to the itaconic acid (signal 4 and 9 at 4.09 and 4.15 ppm) are changing, as new ester bonds with adipic acid are being formed as a result of the transesterification, which have the same chemical shift as the signals of the ester of the unconjugated ester group of the itaconic acid. Furthermore, during the reaction, molecules of ethylene glycol are liberated over time and can also be found in the NMR at 3.73 ppm, which should result in a slight increase of molecular weight of the PEAs. Finally, the signal of the inhibitors can be seen at 6.75 and 3.76 ppm, respectively.

For the PEAs, synthesized via pseudo-one-pot pathway, the NMR spectra also show the characteristic signals described for the first series. However, in all three PEAs, two additional signals appear at 6.80 and 2.32 ppm, which correspond to the mesaconic moieties formed during the condensation product (Figure 2). The mesaconic moiety can be formed at elevated temperatures by isomerization of the itaconic ester in the presence of a base (Scheme 4). This isomerization indicates that during the first step of the reaction, the amine is not completely consumed, and a small amount of free amine is still present in the second reaction step, which is sufficient to catalyze the isomerization. Unfortunately, the free amine was not detectable during the reaction by means of FT-IR. The NMR spectra of the PEA-101 and 102 can be found in the supporting information.

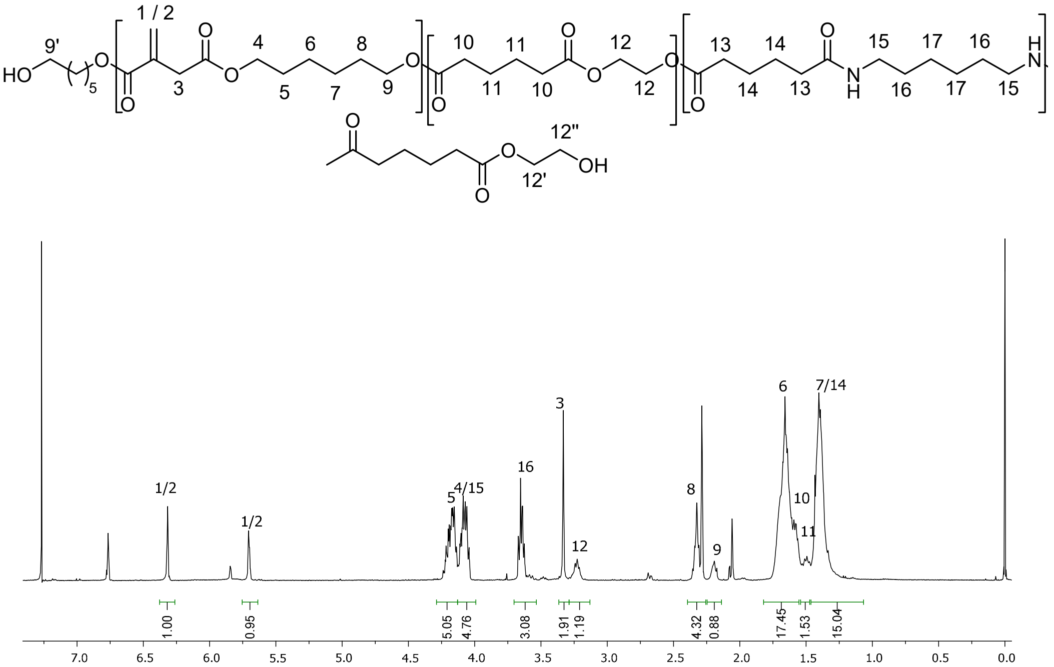
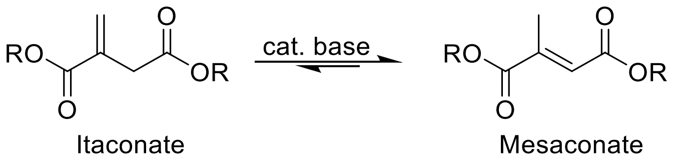


Figure 2. ^{1}H NMR spectra of PEA-103.



Scheme 4. Based-catalyzed isomerization of an itaconate ester to the mesaconate ester.

For the PEAs synthesized via pseudo-one-pot pathway, the NMR spectra also show the characteristic signals described for the first series. Figure 2 shows the NMR spectra of PEA-103. All other spectra can be found in the supporting information.

3.4. GPC Measurements

To gain some insight on the molecular weight distribution of the PEAs synthesized, all polymers were subjected to GPC measurements. The molecular weights of the PEAs are obtained in a gaussian distribution, which is expected for polycondensation reactions. In addition, the PEAs synthesized possess molecular weights of around 300 to 12,000 g/mol, which is reasonable for UV-curing resins. However, as the calibration of the measurements had a cutoff of 575 g/mol, M_n, M_w, and Đ were not calculated, and only the elugram is showed in Figure 3. Furthermore, one of the major challenges associated with the synthesis of resins for UV-curing applications is the undesired premature crosslinking of the reactive double bonds during the polycondensation reaction. This leads to an increase in the molecular weight of the resins and eventually to the gelation of the resins. If such an undesired side reaction would occur, this could be detected by means of GPC analysis trough the appearance of a signal at higher molecular weight, as well as a deviation from the gaussian distribution. In all our cases, no high molecular fraction was observed, indicating that no crosslinking occurred. In addition, all of the PEAs synthesized have similar molecular weight, with slight differences for the second series, where the PEAs with the highest amide content have a slightly higher retention volume and, therefore, lower molecular weight.

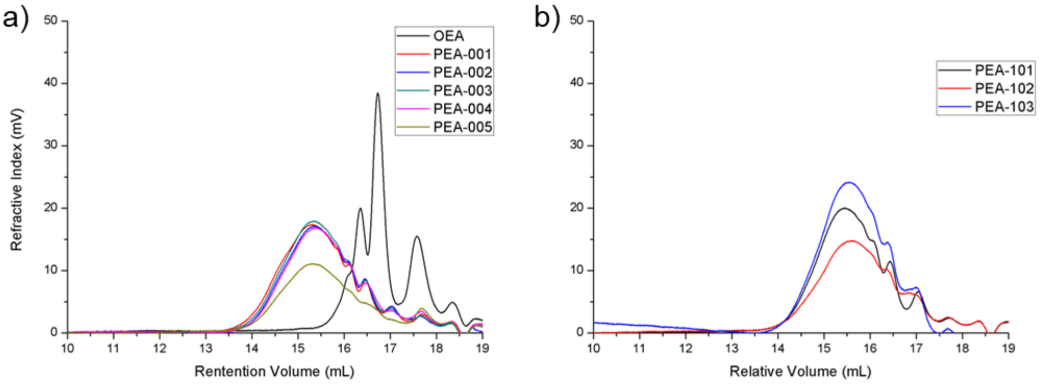


Figure 3. GPC traces of all PEAs synthesized in the course of this study. (a) PEA-001-005; (b) PEA-101-103.

3.5. Viscosity

In addition to GPC, also the viscosities of the resins were closely examined. For coatings applications, the viscosity is an important parameter, as depending on the applications, the resins have to exhibit a certain viscosity to be applicable. If the viscosity is too high, the use of reactive diluents might be necessary. In general, the viscosity is proportional to the molecular weight. However, in the case of polyester amides, the hydrogen bonding induced by the amide groups should also lead to an increase in viscosity. For the PEAs synthesized in this study, the effect can only be seen at amide contents of more than 5%. As a result, a significant increase in viscosity can only be observed for

PEA-005 and PEA-103 with a viscosity of 17.3 and 22.4 Pa.s, respectively (Figure 4a,b). The other PEAs exhibit viscosities of around 6.7–8.2 Pa.s for series one and 4.9–5.9 Pa.s for series two. However, the viscosity of the PEAs drops significantly with increasing temperature, with only slight differences of all PEAs at 75 °C.

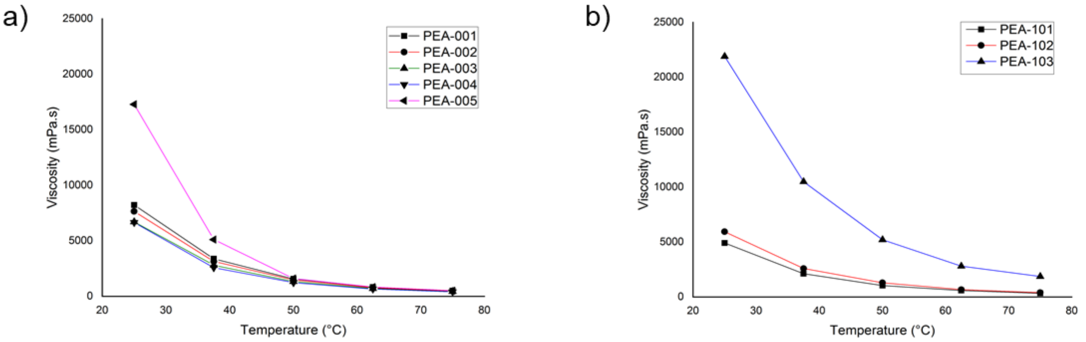


Figure 4. Viscosity curves of PEA synthesized in the course of this study. (a) PEA-001-005; (b) PEA-101-103.

3.6. UV-Curing Behaviour

To study the reactivity of the synthesized PEAs towards UV-curing, the resins were examined by means of Photo-DSC after the addition of 5% of Irgacure 1173 as the photoinitiator. In all cases, the rate of polymerization (ROP) of the PEAs is in the same range as for other UV-curing itaconic acid-based materials [33]. In addition, the ROP of the PEAs is lower than the one obtained from the neat OE. In addition, it decreases with increasing amide content (Figure 5 and Table 3). Both observations can be explained by the fact that the double bond density decreases with an increasing amount of amide. However, there is a major difference between the reactivity of the first and second series. The PEAs obtained by the pseudo-one-pot procedure exhibit reduced reactivity, which can be explained by the lower double bond density, as well as the isomerization to the mesaconate observed by NMR analysis. The internal double bond of the mesaconate is less reactive towards UV-curing compared to the itaconic counterpart. However, despite the lower reactivity, the double bond conversion is, in some cases, higher than for the neat OE. Especially, PEA-003 has a conversion of 71.4% compared to 58% of the neat OE.

Table 3. Overview over double bond density, enthalpy, rate of polymerization, and conversion.

Copolymers	DBD (mmol/g)	ΔH_{theo} (J/g)	ΔH_{exp} (J/g)	C (%)	RoP (s^{-1}/1000)
OE	4.13	250.3	145.3	58.0	21.4
PEA-001	3.92	237.8	135.6	57.0	19.7
PEA-002	3.71	225.3	143.8	63.8	19.6
PEA-003	3.30	200.2	143.0	71.4	17.4
PEA-004	2.89	175.2	120.8	69.0	16.0
PEA-005	2.48	150.2	87.7	58.4	8.5
PEA-101	3.0	151.7	93.9	61.9	7.7
PEA-102	2.5	103.1	59.3	57.5	6.0
PEA-103	1.7	182.0	93.7	51.5	7.2

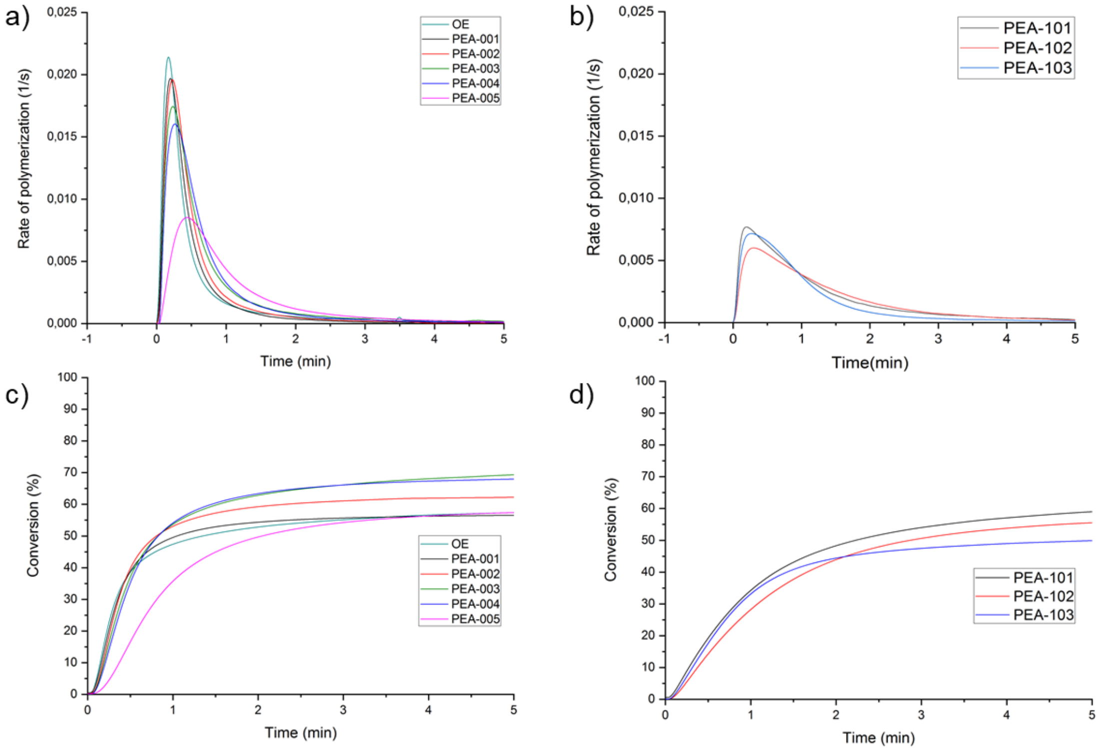


Figure 5. Photo-curing of OE and PEAs. (a) rate of polymerization of PEA-001-005; (b) rate of polymerization of PEA-101-103; (c) free double-bond conversion PEA-001-005; (d) free double-bond conversion PEA-101-103.

The curing of the samples is also visible in the FT-IR spectra before and after curing. Figure 6 shows the FT-IR spectra of PEA-002. The C=C stretch (1639 cm^{-1}) and C=C deformation (816 cm^{-1}) vibrations are significantly reduced after curing.

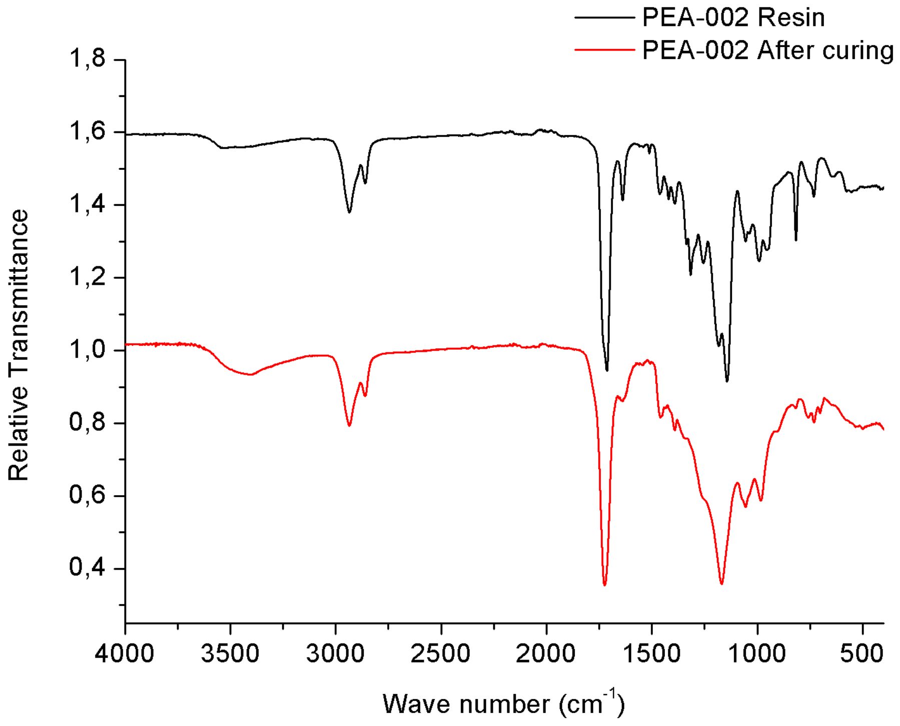


Figure 6. FT-IR-spectra of PEA-002 before and after UV-curing.

In addition to the photo-DSC study, the resins with 5% photo initiator were also applied as films and cured with a radiation dose of 500 mJ/cm^2. The number of curing runs needed to obtain tack-free surface was noted. For the first series, all films, but the last were fully cured after five curing runs. However, only PEA001-003 exhibited a non-sticky surface after curing. The films of the second series were all not fully tack-free after curing (Table 4). This could be a result of the lower reactivity towards UV-curing due to the isomerization of the double bond. Compared to polyester from itaconic acid reported earlier, the reactivity towards UV-curing is lower, especially at high amide content [25]. Figure 7 shows the films obtained from PEA-001 and 003.

Table 4. Curing behavior of PEAs.

PEA	No. of Curing Runs	Surface Appearance
PEA-001	5	dry
PEA-002	5	dry
PEA-003	5	dry
PEA-004	5	sticky
PEA-005	10	very sticky
PEA-101	5	sticky
PEA-102	5	sticky
PEA-103	10	sticky

Figure 7. Pictures of the films obtained after UV-curing. (**a**) PEA-001 and (**b**) PEA-003.

4. Conclusions

In this paper, the first successful synthesis of poly(ester amide)s from itaconic acid is described by two different synthetic approaches. The first series was synthesized via transesterification of an oligoamide and an oligoester that have been separately prepared before. The second series was obtained by a pseudo-one-pot reaction was the diamine was first reacted with dimethyl adipate to obtain the corresponding bis(ester amide). Then IA and HDO were added, and the polycondensation was performed. With both approaches, the aza-Michael addition on the unsaturated double bond followed by a ring formation was suppressed. However, the second synthetic approach led to a significant amount of isomerization from the itaconate to the corresponding mesaconate. The PEA resins were fully characterized and their reactivity towards UV-induced crosslinking was examined by means of Photo-DSC. Even though all PEAs show a reactivity towards UV-curing, all PEAs had a lower rate of polymerization, and films cast were all slower to cure compared to the neat oligoester without any amide moieties. In addition, the viscosity increases significantly especially at amide contents higher than 5 wt%, which can be attributed to the hydrogen bonds between the amide groups. Therefore, these class of bio-based PEAs might not be able to compete with standard polyesters derived from itaconic acid in UV-curing applications. However, in other applications where an increased interaction of the polymer chains is desired, the polymer resins presented in this work might be better suited.

Supplementary Materials: The following are available online at http://www.mdpi.com/2076-3417/10/6/2163/s1, Figure S1—S18.

Author Contributions: T.R., S.A. and M.A. conceived and designed the experiments; R.O. performed the experiments; R.O., T.R. and A.B. analyzed the data; R.O., S.P.A. and T.R. wrote the paper. All authors have read and agreed to the published version of the manuscript

Funding: This research was funded by the Ministry of Higher Education and Scientific Research in Tunisia and the Projekträger Jülich and the Federal Ministry of Education and Research in Germany.

Acknowledgments: The authors would like to thank K. U. Loos und A. J. J. Woortman for the performance of the GPC measurements.

Conflicts of Interest: The authors confirm that this article content has no conflict of interest.

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